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(54) **A process for the production of polyisocyanates containing allophanate and isocyanurate groups.**

(57) The present invention is directed to a process for the production of a polyisocyanate composition having an NCO content of 10 to 47% by weight and a viscosity of less than 2,500 mPa.s, wherein the viscosity is determined from a mixture containing less than 1% by weight of the starting organic diisocyanate, and containing isocyanurate and allophanate groups in a molar ratio of monoisocyanurates to monoallophanates of 10:1 to 1:5 by

- a) catalytically trimerizing a portion of the isocyanate groups of an organic diisocyanate having (cyclo)-aliphatically bound isocyanate groups
- b) adding 0.01 to 0.5 moles, per mole of organic diisocyanate, of a monoalcohol containing 6 to 9 carbon atoms to the organic diisocyanate prior to or during the trimerization reaction of step a) and
- c) terminating the trimerization reaction at the desired degree of trimerization by adding a catalyst poison and/or by thermally deactivating the catalyst,

wherein said trimerization catalyst is a compound containing aminosilyl groups or a catalyst which is capable of reducing the isocyanate content of a mixture consisting of 1,6-hexamethylene diisocyanate containing less than 10 ppm of carbon dioxide and the trimerization catalyst from 50% to 45% by weight or less within a period of 4 hours at a catalyst concentration of 500 ppm, based on the weight of 1,6-hexamethylene diisocyanate, and a temperature of 80° C.

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## BACKGROUND OF THE INVENTION

### Field of the Invention

5 The present invention is directed to a process for the production of polyisocyanates which contain allophanate groups and isocyanurate groups and have a low viscosity and improved compatibility with polar and slightly polar solvents and isocyanate-reactive components.

### Description of the Prior Art

10 Polyisocyanates containing isocyanurate groups are known and disclosed in U.S. Patents 3,487,080, 3,996,223, 4,324,879 and 4,412,073. While these polyisocyanates possess many outstanding properties, they do require improvement in two areas. First, the viscosity of commercially available polyisocyanates containing isocyanurate groups needs to be reduced in order to reduce the amount of solvent which is  
15 necessary to obtain a suitable processing viscosity. Presently, there are an increasing number of government regulations which limit the amount of volatile solvents which may be present in coating systems. Therefore, isocyanurate group-containing polyisocyanates may be precluded from certain applications because it is not possible to reduce the viscosity of these polyisocyanates to a suitable processing viscosity without using high amounts of solvent. Second, the isocyanurate group-containing polyisocyanates do not  
20 possess sufficient compatibility with highly branched polyester co-reactants as evidenced by the gloss and distinctness of image readings obtained from coatings prepared from these reactants.

It has been proposed in U.S. Patent 4,801,663 to reduce the viscosity of isocyanurate group-containing polyisocyanates prepared from 1,6-hexamethylene diisocyanate (HDI). By terminating the reaction at a very low degree of trimerization higher contents of the monoisocyanurate of HDI are obtained and the quantity of  
25 polyisocyanates containing more than one isocyanurate ring is reduced. Because these latter polyisocyanates have a much higher viscosity than the monoisocyanurate, the resulting polyisocyanates have a reduced viscosity. However, a significant disadvantage of this system is that because the reaction is terminated at a very low degree of trimerization, the overall yield is very low and the amount of HDI which must be separated from the product is substantially increased. In other words the small reduction in  
30 viscosity is offset by a significant increase in the production cost of the product. Further, the resulting product does not possess optimum compatibility with highly branched polyester resins.

Accordingly, it is an object of the present invention to provide polyisocyanates which have a reduced viscosity and improved compatibility with crosslinked polyester co-reactants, while possessing the desirable properties of known polyisocyanates containing isocyanurate groups. It is an additional object of the present  
35 invention to provide polyisocyanates which may be produced at reasonable production costs and which are obtained in high yields. Surprisingly, these objectives may be achieved in accordance with the present invention as described hereinafter by the incorporation of specific monoalcohols before or during the trimerization process in order to produce a polyisocyanate containing isocyanurate and allophanate groups.

U.S. Patents 4,582,888, 4,604,418, 4,647,623, 4,789,705 are directed the incorporation of various diols  
40 in order to improve the compatibility of the resulting polyisocyanates with certain solvents and co-reactants. While the use of diols may improve the compatibility of the polyisocyanates, the diols do not reduce the viscosity of the polyisocyanates for a given yield.

Many of these references as well as those previously set forth disclose the use of monoalcohols or glycols as co-catalysts for the trimerization reaction. However, none of these references suggest the  
45 incorporation of allophanate groups to reduce the viscosity of polyisocyanates containing isocyanurate groups. Further, these references teach that the use of these cocatalysts should be kept to a minimum since the resulting urethane groups reduce the drying time of coatings prepared from the polyisocyanates. In particular, U.S. Patent 4,582,888 cautions against the use of any amount of monoalcohol which is in excess of that needed to dissolve the catalyst.

50 Japanese Publication 61-151179 discloses the use of monoalcohols containing 6 to 9 carbon atoms as to-catalysts for trimerization catalysts which do not trimerize HDI in the absence of a co-catalyst. This reference does not suggest the use of these monoalcohols in combination with trimerization catalysts which are effective for the trimerization reaction in the absence of co-catalysts.

### 55 SUMMARY OF THE INVENTION

The present invention is directed to a process for the production of a polyisocyanate composition having an NCO content of 10 to 47% by weight and a viscosity of less than 2,500 mPa.s, wherein the

viscosity is determined from a mixture containing less than 1% by weight of the starting organic diisocyanate, and containing isocyanurate and allophanate groups in a molar ratio of monoisocyanurates to monoallophanates of 10:1 to 1:5 by

- a) catalytically trimerizing a portion of the isocyanate groups of an organic diisocyanate having (cyclo)-  
5 aliphatically bound isocyanate groups
  - b) adding 0.01 to 0.5 moles, per mole of organic diisocyanate, of a monoalcohol containing 6 to 9 carbon atoms to the organic diisocyanate prior to or during the trimerization reaction of step a) and
  - c) terminating the trimerization reaction at the desired degree of trimerization by adding a catalyst poison and/or by thermally deactivating the catalyst,
- 10 wherein the trimerization catalyst is a compound containing aminosilyl groups or a catalyst which is capable of reducing the isocyanate content of a mixture consisting of 1,6-hexamethylene diisocyanate containing less than 10 ppm of carbon dioxide and the trimerization catalyst from 50% to 45% by weight or less within a period of 4 hours at a catalyst concentration of 500 ppm, based on the weight of 1,6-hexamethylene diisocyanate, and a temperature of 80 °C.

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#### DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention the term "monoisocyanurate" means a polyisocyanate containing one isocyanurate group and formed from three diisocyanate molecules, and the term  
20 "polyisocyanurate" means a polyisocyanate containing more than one isocyanurate group. The term "monoallophanate" means a polyisocyanate containing one allophanate group and formed from two diisocyanate molecules and 1 monoalcohol molecule, and the term "polyallophanate" means a polyisocyanate containing more than one allophanate group. The term "(cyclo)aliphatically bound isocyanate groups" means aliphatically and/or cycloaliphatically bound isocyanate groups.

25 Examples of suitable diisocyanates to be used as starting materials for preparing the polyisocyanates according to the present invention are organic diisocyanates represented by the formula



30 wherein R represents an organic group obtained by removing the isocyanate groups from an organic diisocyanate having (cyclo)aliphatically bound isocyanate groups and a molecular weight of 112 to 1,000, preferably 140 to 400. Preferred diisocyanates for the process according to the invention are those represented by the above formula wherein R represents a divalent aliphatic hydrocarbon group having from 4 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon group having from 5 to 15 carbon atoms or a  
35 divalent araliphatic hydrocarbon group having from 7 to 15 carbon atoms. Examples of the organic diisocyanates which are particularly suitable for the process include 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylenediisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)-methane, 1,3- and 1,4-bis(isocyanatomethyl)-cyclohexane, bis-(4-  
40 isocyanato-3-methyl-cyclohexyl)-methane,  $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3- and/or -1,4-xylylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, and 2,4- and/or 2,6-hexahydrotoluylene diisocyanate. Mixtures of diisocyanates may also be used. Preferred diisocyanates are 1,6-hexamethylene diisocyanate, isophorone diisocyanate and bis-(4-isocyanatocyclohexyl)-methane. 1,6-hexamethylene  
45 diisocyanate (HDI) is especially preferred.

It is also possible in accordance with the present invention to use blends of the previously mentioned diisocyanates with monoisocyanates or polyisocyanates having 3 or more isocyanate groups, provided that the isocyanate groups are (cyclo)aliphatically bound.

In accordance with the present invention it is preferred to treat the starting diisocyanates by bubbling an  
50 inert gas such as nitrogen through the starting diisocyanate in order to reduce the content of carbon dioxide. This process is discussed in German Offenlegungsschrift 3,806,276 (U.S. Application, Serial No. 07/311,920).

Trimerization catalysts which are suitable for the process according to the invention include compounds containing aminosilyl groups and those which are effective for the trimerization of polyisocyanates in the  
55 absence of a co-catalyst containing urethane groups, with the exception of phosphines, e.g., those described in DE-OS 1,935,763, and Mannich bases, for example, those based on nonylphenol, formaldehyde and dimethylamine of the type described in U.S. Patents 3,996,223 and 4,115,373. The phosphines, in addition to promoting the trimerization reaction, also promote the dimerization of diisocyanates. The

Mannich bases are generally used for the trimerization of aromatic polyisocyanates and are much less effective or not effective at all for the trimerization of (cyclo)aliphatic diisocyanates. Therefore, these catalysts are not suitable for preparing the products of the present invention. The trimerization catalysts should also catalyze the formation of allophanate groups from urethane groups.

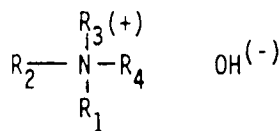
5 Compounds containing aminosilyl groups such as aminosilanes, diaminosilanes, silylureas and silazanes are described in U.S. Patent 4,412,073, the disclosure of which is herein incorporated by reference;

Catalysts which are effective for the trimerization of diisocyanates in the absence of a co-catalyst may be defined as those which are capable of reducing the isocyanate content of a mixture consisting of 1,6-hexamethylene diisocyanate containing less than 10 ppm of carbon dioxide and the trimerization catalyst  
10 from 50% to 45% by weight or less within a period of 4 hours at a catalyst concentration of 500 ppm, based on the weight of 1,6-hexamethylene diisocyanate, and a temperature of 80°C. Examples of these catalysts are known and include alkali phenolates of the type described in GB-PS 1,391,066 or GB-PS 1,386,399; aziridine derivatives in combination with tertiary amines of the type described in U.S. Patent 3,919,218, the disclosure of which is herein incorporated by reference; quaternary ammonium carboxylates  
15 of the type described in U.S. Patents 4,454,317 and 4,801,663, the disclosures of which are herein incorporated by reference;

quaternary ammonium phenolates with a zwitterionic structure of the type described in U.S. Patent 4,335,219, the disclosure of which is herein incorporated by reference; ammonium phosphonates and phosphates of the type described in U.S. Patent 4,499,253, the disclosure of which is herein incorporated  
20 by reference; alkali carboxylates of the type described in U.S. Patent 4,604,418, the disclosure of which is herein incorporated by reference; basic alkali metal salts complexed with acyclic organic compounds as described in U.S. Patent 4,379,905, the disclosure of which is herein incorporated by reference, such as potassium acetate complexed with a polyethylene glycol which contains an average of 5 to 8 ethylene oxide units; basic alkali metal salts complexed with crown ethers as described in U.S. Patent 4,487,928, the  
25 disclosure of which is herein incorporated by reference; and mixtures of alkali metal fluorides and quaternary ammonium or phosphonium salts as described in U.S. Patent 4,960,848, the disclosure of which is herein incorporated by reference.

Particularly suitable catalysts which are effective for the trimerization of diisocyanates in the absence of a co-catalyst are quaternary ammonium hydroxides corresponding to the formula

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as described in U.S. Patent 4,324,879 and German Offenlegungsschriften 2,806,731 and 2,901,479. Preferred quaternary ammonium hydroxides are those wherein the radicals  $R_1$  to  $R_4$  represent identical or  
40 different alkyl groups having from 1 to 20, preferably from 1 to 4 carbon atoms, which may optionally be substituted by hydroxyl groups. Two of the radicals  $R_1$  to  $R_4$  may form a heterocyclic ring having from 3 to 5 carbon atoms together with the nitrogen atom and optionally with a further nitrogen or oxygen atom. Also the radicals  $R_1$  to  $R_3$  in each case may represent ethylene radicals which form a bicyclic triethylene  
45 diamine structure together with the quaternary nitrogen atom and a further tertiary nitrogen atom, provided that the radical  $R_4$  then represents a hydroxyalkyl group having from 2 to 4 carbon atoms in which the hydroxyl group is preferably arranged in a 2-position to the quaternary nitrogen atom. The hydroxyl-substituted radical or the hydroxyl-substituted radicals may also contain other substituents, particularly  $C_1$  to  $C_4$ -alkoxy substituents.

The production of these quaternary ammonium catalysts takes place in known manner by reacting a  
50 tertiary amine with an alkylene oxide in an aqueous-alcoholic medium (c.f. US-P 3,995,997, col. 2, lines 19-44). Examples of suitable tertiary amines include trimethylamine, tributylamine, 2-dimethylaminoethanol, triethanolamine, dodecyltrimethylamine, N,N-dimethylcyclohexylamine, N-methylpyrrolidine, N-methylmorpholine and 1,4-diazabicyclo-[2,2,2]-octane. Examples of suitable alkylene oxides include ethylene oxide, propylene oxide, 1,2-butylene oxide, styrene oxide and methoxy, ethoxy or phenoxy propylene oxide. The  
55 most preferred catalysts from this group are N,N,N-trimethyl-N-(2-hydroxyethyl)-ammonium hydroxide and N,N,N-trimethyl-N-(2-hydroxypropyl)-ammonium hydroxide. Another most preferred catalyst is N,N,N-trimethyl-N-benzyl-ammonium hydroxide.

The trimerization of the starting diisocyanates may be carried out in the absence or in the presence of

solvents which are inert to isocyanate groups. Depending on the area of application of the products according to the invention, low to medium-boiling solvents or high-boiling solvents can be used. Suitable solvents include esters such as ethyl acetate or butyl acetate; ketones such as acetone or butanone; aromatic compounds such as toluene or xylene; halogenated hydrocarbons such as methylene chloride and trichloroethylene; ethers such as diisopropylether; and alkanes such as cyclohexane, petroleum ether or ligroin.

The trimerization catalysts are generally used in quantities of about 0.0005 to 5% by weight, preferably about 0.002 to 2% by weight, based on the diisocyanate used. If, for example, a preferred catalyst such as N,N,N-trimethyl-N-(2-hydroxypropyl)-ammonium hydroxide is used, then quantities of about 0.0005 to 1% by weight, preferably about 0.001 to 0.02 by weight, based on starting diisocyanate, are generally sufficient. The catalysts may be used in pure form or in solution. The previously named solvents which are inert to isocyanate groups are suitable as solvents, depending on the type of catalysts. Dimethyl formamide or dimethyl sulphoxide may also be used as solvents for the catalysts.

The simultaneous use of co-catalysts is possible in the process according to the invention, but not necessary. All substances from which a polymerizing effect on isocyanates is known are suitable as co-catalysts such as those described in DE-OS 2,806,731. The co-catalysts are optionally used in a lesser amount on a weight basis in relation to the amount of the trimerization catalyst.

In accordance with the present invention urethane groups and subsequently allophanate groups are incorporated into the polyisocyanates by the use of monoalcohols. The monoalcohols may be linear, branched or cyclic and contain 6 to 9, preferably 6 or 8 carbon atoms. The monoalcohols may optionally contain ether groups. Examples of suitable monoalcohols include n-hexanol, n-heptanol, n-octanol, n-nonanol, 2-ethyl hexanol, trimethyl hexanol, cyclohexanol and benzyl alcohol. The molar ratio of monoalcohol to diisocyanate is about 0.01 to 0.5, preferably about 0.04 to 0.2.

The reaction temperature for isocyanurate and allophanate formation in accordance with the present invention is about 10 to 160 °C, preferably about 50 to 150 °C and more preferably about 90 to 120 °C.

The process according to the invention may take place either batchwise or continuously, for example, as described below. The starting diisocyanate is introduced with the exclusion of moisture and optionally with an inert gas into a suitable stirred vessel or tube and optionally mixed with a solvent which is inert to isocyanate groups such as toluene, butyl acetate, diisopropylether or cyclohexane. The previously described monoalcohol may be introduced into the reaction vessel in accordance with several embodiments. The monoalcohol may be prereacted with the diisocyanate to form urethane groups prior to introducing the diisocyanate into the reaction vessel; the monoalcohol may be mixed with the diisocyanate and introduced into the reaction vessel; the monoalcohol may be separately added to the reaction vessel either before or after, preferably after, the diisocyanate is added; or the catalyst may be dissolved in the monoalcohol prior to introducing the solution into the reaction vessel.

The polyisocyanates according to the invention may also be prepared by blending polyisocyanates containing isocyanurate groups with monoallophanates.

At a temperature of about 60 °C and in the presence of the required catalyst or catalyst solution the trimerization begins and is indicated by an exothermic reaction. As the reaction temperature increases the conversion rate of urethane groups to allophanate groups increases faster than the formation of isocyanurate groups. At temperatures above 85 °C when the desired degree of trimerization is achieved, the urethane groups are generally completely converted to allophanate groups and the product, after removal of unreacted monomer and any solvent present has a low viscosity relative to the yield which is obtained. At temperatures below 85 °C at the same degree of isocyanate group consumption, some urethane groups remain unconverted and the product has a slightly higher, but still low viscosity relative to the yield which is obtained. The progress of the reaction is followed by determining the NCO content by a suitable method such as titration, refractive index or IR analysis. Thus, the reaction may be terminated at the desired degree of trimerization. The termination of the trimerization reaction can take place, for example, at an NCO content of about 15% to 47%, preferably about 20 to 40%.

The termination of the trimerization reaction can take place, for example, by the addition of a catalyst-poison of the type named by way of example in the above-mentioned literature references. For example, when using basic catalysts the reaction is terminated by the addition of a quantity, which is at least equivalent to the catalyst quantity, of an acid chloride such as benzoyl chloride. When using heat-labile catalysts, for example, the previously described quaternary ammonium hydroxides, poisoning of the catalyst by the addition of a catalyst-poison may be dispensed with, since these catalysts decompose in the course of the reaction. When using such catalysts, the catalyst quantity and the reaction temperature are preferably selected such that the catalyst which continuously decomposes is totally decomposed when the desired degree of trimerization is reached. The quantity of catalyst or reaction temperature which is necessary to

achieve this decomposition can be determined by a preliminary experiment. It is also possible initially to use a lesser quantity of a heat sensitive catalyst than is necessary to achieve the desired degree of trimerization and to subsequently catalyze the reaction by a further incremental addition of catalyst, whereby the quantity of catalyst added later is calculated such that when the desired degree of trimerization is achieved, the total quantity of catalyst is spent. The use of suspended catalysts is also possible. These catalysts are removed after achieving the desired degree of trimerization by filtering the reaction mixture.

The working-up of the reaction mixture, optionally after previous separation of insoluble catalyst constituents, may take place in various ways depending upon how the reaction was conducted and the area of application for the isocyanates. It is possible to use the polyisocyanates according to the invention which have been produced in solution directly as a lacquer raw material, without a purification stage, if it is not necessary to reduce the free monomer content. Any solvent used during trimerization reaction and any unreacted monomer present in the polyisocyanate product can also be removed by distillation in known manner. The product generally contains a total of less than 2, preferably less than 1% of free (unreacted) monomeric diisocyanates. The products according to the invention have a viscosity of less than 10,000 mPa.s, preferably less than 2000 mPa.s and more preferably less than 1300 mPa.s.

The products according to the present invention are polyisocyanates containing isocyanurate groups and allophanate groups. The products may also contain residual urethane groups which have not been converted to allophanate groups depending upon the temperature maintained during the reaction and the degree of isocyanate group consumption. The ratio of monoisocyanurate groups to monoallophanate groups present in the polyisocyanates according to the invention is about 10:1 to 1:5, preferably about 5:1 to 1:2.

The products according to the invention are valuable starting materials for the production of polyisocyanate polyaddition products by reaction with compounds containing at least two isocyanate reactive groups. Preferred products are most preferably one or two-component polyurethane coatings.

Preferred reaction partners for the products according to the invention, which may optionally be present in blocked form, are the polyhydroxy polyesters, polyhydroxy polyethers, polyhydroxy polyacrylates and optionally low molecular weight, polyhydric alcohols known from polyurethane coatings technology. Polyamines, particularly in blocked form, for example as polyketimines or oxazolidines are also suitable reaction partners for the products according to the invention. The amounts of the polyisocyanates according to the invention and their reaction partners are selected to provide equivalent ratio of isocyanate groups (whether present in blocked or unblocked form) to isocyanate-reactive groups of about 0.8 to 3, preferably about 0.9 to 1.1.

To accelerate hardening, the coating compositions may contain known polyurethane catalysts, e.g., tertiary amines such as triethylamine, pyridine, methyl pyridine, benzyl dimethylamine, N,N-dimethylamino cyclohexane, N-methylpiperidine, pentamethyl diethylene triamine, 1,4-diazabicyclo[2,2,2]octane and N,N'-dimethyl piperazine; or metal salts such as iron(III)-chloride, zinc chloride, zinc-2-ethyl caproate, tin(II)-ethyl caproate, dibutyltin(IV)-dilaurate and molybdenum glycolate.

The products according to the invention are also valuable starting materials for two-component polyurethane stoving enamels in which the isocyanate groups are used in a form blocked by known blocking agents. The blocking reaction is carried out in known manner by reacting the isocyanate groups with suitable blocking agents, preferably at an elevated temperature (e.g. about 40 to 160 °C), and optionally in the presence of a suitable catalyst, for example, the previously described tertiary amines or metal salts.

Suitable blocking agents include monophenols such as phenol, the cresols, the trimethylphenols and the tert. butyl phenols; tertiary alcohols such as tert. butanol, tert. amyl alcohol and dimethylphenyl carbinol; compounds which easily form enols such as acetoacetic ester, acetyl acetone and malonic acid derivatives, e.g. malonic acid diethylester; secondary aromatic amines such as N-methyl aniline, the N-methyl toluidine, N-phenyl toluidine and N-phenyl xylydine; imides such as succinimide; lactams such as  $\epsilon$ -caprolactam and  $\delta$ -valerolactam; oximes such as butanone oxime and cyclohexanone oxime mercaptans such as methyl mercaptan, ethyl mercaptan, butyl mercaptan, 2-mercaptobenzthiazole,  $\alpha$ -naphthyl mercaptan and dodecyl mercaptan; and triazoles such as 1H-1,2,4-triazole.

The coating compositions may also contain other additives such as pigments, dyes, fillers, levelling agents and solvents. The coating compositions may be applied to the substrate to be coated in solution or from the melt by conventional methods such as painting, rolling, pouring or spraying.

The coating compositions containing the polyisocyanates according to the invention provide coatings which adhere surprisingly well to a metallic base, and are particularly light-fast, color-stable in the presence of heat and very resistant to abrasion. Furthermore, they are characterized by high hardness, elasticity, very good resistance to chemicals, high gloss, excellent weather resistance and good pigmenting qualities. The polyisocyanates according to the invention also possess good compatibility with highly branched polyester resins.

The invention is further illustrated, but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified. The use of ppm in the tables refers to the amount of catalyst excluding solvent.

5    EXAMPLES

EXAMPLE 1

      To a 500 ml 3-neck flask equipped with a gas bubbler, mechanical stirrer, thermometer and condenser  
10    were added 300 grams of hexamethylene diisocyanate and 23.1 grams of 2-octanol. Dry nitrogen was  
      bubbled through the stirred reaction mixture while it was heated at 60 ° C. When the urethane reaction was  
      complete (about 1 hour), the temperature was raised to 90 ° C. To the reaction mixture at 90 ° C were added  
      0.294 grams of a 4.4% solution of trimethylbenzylammonium hydroxide dissolved in 2-butanol. The reaction  
      temperature was maintained between 90 and 100 ° C. When the reaction mixture reached an NCO content of  
15    34.2%, the reaction was stopped by adding 0.294 grams of di-(2-ethylhexyl) phosphate. The excess  
      monomer was removed by thin film evaporation to provide an almost colorless, clear liquid having a  
      viscosity of 720 mPa.s (25 ° C), an NCO content of 19.0%, and a free monomer (HDI) content of 0.2%. The  
      yield, which was calculated by determining the % free HDI of the product before distillation, was 49.1%.

20    EXAMPLES 2 - 6

      To the equipment described above was added the indicated ratio of alcohol to hexamethylene  
      diisocyanate set forth in Table 1. The stirred mixture was heated to the indicated reaction temperature over  
      a period of 1 to 2 hours while dry nitrogen was bubbled through the reaction mixture. The catalyst solution  
25    (trimethylbenzyl ammonium hydroxide) was added to the reaction mixture and the mixture was kept at the  
      indicated temperature until the NCO content labeled as "crude NCO" was reached. The reaction was  
      stopped by adding an equimolar di-(2 ethylhexyl) phosphate relative to the catalyst. The excess monomer  
      was removed by thin layer evaporation to provide clear products with the properties set forth in Table 1.

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TABLE I

Example No.	Alcohol/ Weight*	Catalyst (ppm)	Reaction Temp.	Stripped Product			
				Crude NCO	% HDI	Viscosity mPa.s, 25°C	NCO % Yield
2	2-ethyl hexanol 4.0	76	50	41.9	0.2	770	20.8 20%
3	1-octanol 4.4	179	90	37.3	0.5	780	20.6 43
4	1-octanol 7.7	174	90	34.0	0.4	750	18.4 52
5	3-octanol 4.4	171	90	37.2	0.5	1070	20 43
6	3-octanol 7.7	211	90	34.3	0.5	990	17.9 50

\* Weight of alcohol per 100 parts of HDI

## EXAMPLE 7

To a 500 ml 3-neck flask equipped with a gas bubbler, mechanical stirrer, thermometer and condenser were added 334 grams of hexamethylene diisocyanate and 21.0 grams of benzyl alcohol. Dry nitrogen was bubbled through the stirred reaction mixture while it was heated at 60°C. When the urethane reaction was complete (about 1 hour), the temperature was raised to 90°C. To the reaction mixture at 90°C were added 0.24 grams of a 4.4% solution of trimethylbenzylammonium hydroxide dissolved in 1-butanol. The reaction temperature was maintained between 90 and 100°C. When the reaction mixture reached an NCO content of 35.0%, the reaction was stopped by adding 0.24 grams of di-(2-ethylhexyl) phosphate. The excess monomer was removed by thin film evaporation to provide an almost colorless, clear liquid having a viscosity of 610 mPa.s (25°C), an NCO content of 18.6%, and a free monomer (HDI) content of 0.1%. The yield, which was calculated by determining the % free HDI of the product before distillation, was 34.4%.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those



skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

# Claims

- 5 1. A process for the production of a polyisocyanate composition having an NCO content of 10 to 47% by weight and a viscosity of less than 2,500 mPa.s, wherein the viscosity is determined from a mixture containing less than 1% by weight of the starting organic diisocyanate, and containing isocyanurate and  
10 allophanate groups in a molar ratio of monoisocyanurates to monoallophanates of 10:1 to 1:5 which comprises
  - a) catalytically trimerizing a portion of the isocyanate groups of an organic diisocyanate having (cyclo)aliphatically bound isocyanate groups in the presence of a trimerization catalyst,
  - b) adding 0.01 to 0.5 moles, per mole of said organic diisocyanate, of a monoalcohol containing 6 to  
15 9 carbon atoms to said organic diisocyanate prior to or during the trimerization reaction of step a) and
  - c) terminating the trimerization reaction at the desired degree of trimerization by adding a catalyst poison and/or by thermally deactivating the catalyst,wherein said trimerization catalyst comprises a compound containing aminosilyl groups or a catalyst which is capable of reducing the isocyanate content of a mixture consisting of 1,6-hexamethylene  
20 diisocyanate containing less than 10 ppm of carbon dioxide and the trimerization catalyst from 50% to 45% by weight or less within a period of 4 hours at a catalyst concentration of 500 ppm, based on the weight of 1,6-hexamethylene diisocyanate, and a temperature of 80 °C.
- 25 2. The process of Claim 1 wherein said organic diisocyanate comprises 1,6-hexamethylene diisocyanate.
3. The process of Claim 1 or 2 wherein said monoalcohol contains 6 or 8 carbon atoms.
4. The process of Claim 1 or 2 wherein said monoalcohol comprises 2-ethyl hexanol.
- 30 5. A process for the production of a polyisocyanate composition having an NCO content of 10 to 47% by weight and a viscosity of less than 1,500 mPa.s, wherein the viscosity is determined from a mixture containing less than 1% by weight of the starting organic diisocyanate, and containing isocyanurate and allophanate groups in a molar ratio of monoisocyanurates to monoallophanates of 10:1 to 1:5 which comprises
  - 35 a) catalytically trimerizing a portion of the isocyanate groups of an organic diisocyanate having (cyclo)aliphatically bound isocyanate groups in the presence of a trimerization catalyst,
  - b) adding 0.01 to 0.5 moles, per mole of said organic diisocyanate, of a monoalcohol containing 6 to 9 carbon atoms to said organic diisocyanate prior to or during the trimerization reaction of step a) and
  - 40 c) terminating the trimerization reaction at the desired degree of trimerization by adding a catalyst poison and/or by thermally deactivating the catalyst,wherein said trimerization catalyst comprises a compound containing aminosilyl groups or a catalyst which is capable of reducing the isocyanate content of a mixture consisting of 1,6-hexamethylene diisocyanate containing less than 10 ppm of carbon dioxide and the trimerization catalyst from 50% to  
45 45% by weight or less within a period of 4 hours at a catalyst concentration of 500 ppm, based on the weight of 1,6-hexamethylene diisocyanate, and a temperature of 80 °C.
6. The process of Claim 5 wherein said organic diisocyanate comprises 1,6-hexamethylene diisocyanate.
- 50 7. The process of Claim 5 or 6 wherein said monoalcohol contains 6 or 8 carbon atoms.
8. The process of Claim 7 or 8 wherein said monoalcohol comprises 2-ethyl hexanol.
9. The process of Claims 5 to 8 wherein said trimerization catalyst comprises a member selected from the  
55 group consisting of quaternary ammonium hydroxides, quaternary ammonium fluorides, quaternary ammonium carboxylates, alkali metal carboxylates and compounds containing aminosilyl groups.



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# EUROPEAN SEARCH REPORT

Application Number

EP 92 11 1701

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	FR-A-1 304 301 (I.C.I.) *abstract points A,A1,A4* * page 1, right column, paragraph 4 * * page 2, left column, paragraph 5 * ---	1	C08G18/02 C08G18/79 C08G18/78 C07D251/34
A	GB-A-840 318 (BAYER) * claims 1-3 * * page 1, line 80 - line 87 * * page 2, line 4 - line 36 * * page 2, line 69 - line 99 * ---	1	
A	GB-A-994 890 (I.C.I.) * claims 1,2,4,5 * * page 2, line 1 - line 27 * ---	1	
A	EP-A-0 416 338 (BAYER) * claims 1-3,5 * * page 4, line 13 - line 30 * ---	1	
A	FR-A-1 215 428 (BASF) *abstract points I1,I2* * page 1, right column, paragraph 2 * * page 2, right column, paragraph 2 -paragraph 3 * ---	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5)  C08G C07D
A	EP-A-0 057 653 (RHONE-POULENC) * claims 1,8-11 * ---	1	
D	& US-A-4 412 073 ---		
A	EP-A-0 003 765 (BAYER) * claims 1,2,4 * -----	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05 NOVEMBER 1992	Examiner VAN PUYMBROECK M. A.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	